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**“COMBINATION OF A LOW ASH LUBRICATING  
OIL COMPOSITION AND LOW SULFUR FUEL”**

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**Inventor(s):**

**Stephen ARROWSMITH  
Alisdair J. BROWN**

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**COMBINATION OF A LOW ASH LUBRICATING OIL COMPOSITION**  
**AND LOW SULFUR FUEL**

5       The present invention relates to low-ash lubricating oil compositions for use in, or used in, engines operated by low-sulphur fuels, which oil compositions provide improved lubricant properties, particularly improved lead corrosion protection and improved compatibility with engines equipped with particulate traps.

**BACKGROUND OF THE INVENTION**

10       Environmental concerns have led to continued efforts to reduce the particulate emissions of vehicular internal combustion engines, particularly compression ignited (diesel) internal combustion engines. One technology being used to reduce particulate emissions of diesel engines is the particulate trap, which is to be incorporated into all  
15       passenger car and heavy duty diesel vehicles designed to comply with the requirements of Euro IV emissions legislation. When lubricant is consumed during use in the engine, ash derived from metal-containing additives in the lubricant, primarily from metal-containing detergents and antiwear agents, accumulate in the particulate trap. This ash cannot be purged without removing the trap from the engine  
20       and cleaning either *via* washing or blowing the ash from the particulate trap with compressed air. Ash allowed to accumulate in the particulate trap may cause an increase in pressure behind the trap (back pressure). If this back pressure becomes severe, internal exhaust gas recirculation may occur with a resulting loss of fuel economy and eventual engine failure. Because lubricants require acid neutralization  
25       (provided by detergents), and wear protection (provided by ZDDP), metal-containing additives that form ash upon use in engines cannot simply be removed.

30       Concurrently, to provide compatibility with exhaust catalyst systems, there has been a move to fuels containing lower sulphur contents. While fuels used in the United States presently may contain up to 400 ppm or more of sulphur, reduced sulphur fuels containing no more than 50 ppm are now in use in Europe, and the trend toward even lower sulphur fuels (>15 ppm) continues. Further, for both environmental reasons, and to ensure proper functioning of catalytic converters and

certain aftertreatment devices such as exhaust gas recirculation (EGR) systems, particularly in heavy duty diesel applications, future lubricating oil specifications (ACEA E6 in Europe, PC-10 in the United States) will most likely require lubricating oil compositions to contain reduced amounts of phosphorus and sulphur.

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The use of reduced amounts of ZDDP, in combination with low sulphur fuels is described in WO 02/18521. In WO 02/18521, it is noted that in spite of the reduced lubricity of low-sulphur fuels, the amount of metal-containing antiwear agent, particularly ZDDP can be reduced while maintaining adequate wear performance.

10 While reducing the amount of added ZDDP will reduce the ash content of the lubricant, WO 02/18521 does not suggest the use of lubricants in which ash content is minimized by reducing the amount of other metal-containing additives, particularly metal-containing detergents.

15 Therefore, it would be advantageous to identify other means for reducing the amount of metal-containing additives, and thus, the ash content of lubricating oil compositions used in combination with low sulphur fuels, such that said lubricating oil compositions are more suitable for use in engines provided with particulate traps.

20 Engine combustion generates nitrogen oxide gases ( $\text{NO}_x$ ). Further, when sulphur-containing fuel is burned in the engine, the sulphur is converted to sulphur oxide gases ( $\text{SO}_x$ ). In addition, one of the major by-products of the combustion of a hydrocarbon fuel is water vapor. When the  $\text{NO}_x$  and  $\text{SO}_x$  gases react with the water vapor mineral acids are formed. A portion of the mineral acids becomes introduced  
25 into the lubricants *via* blow-by causing engine corrosion. These problems are exacerbated in engines in which emissions are reduced by means of exhaust gas recirculation (EGR) systems, particularly EGR systems in which exhaust gases and/or combustion air is cooled prior to introduction into the engine combustion chamber. Acids, including mineral acids, are neutralized by the action of detergents in the  
30 lubricant.

It was previously believed that NO<sub>x</sub> gases were the major contributor to acids that cause corrosion in the engine because of the greater proportion of NO<sub>x</sub> gases compared to other mineral acid forming gases (see Figure 1). The amount of SO<sub>x</sub> gases was considered a lesser concern since many typical fuels contain only about 400 ppm of sulphur, and reducing the sulphur content to, for example 50 ppm, does not result in a significant reduction in the overall amount of acid in the lubricant. Therefore, it was believed that a reduction in the amount of sulphur in the fuel would not have a significant impact in the amount of detergent needed to neutralize acid in the lubricant. Surprisingly, it has now been found that acids derived from fuel sulphur are a major contributor to engine corrosion and the amount of sulphur in the fuel has a greater than expected impact on engine corrosion. Therefore, unexpectedly, the amount of detergent needed to neutralize mineral acids generated during combustion and ameliorate engine corrosion can be reduced dramatically in engines operated by low sulphur fuels. The use of reduced levels of metal-containing detergents allows for the formulation of low ash content lubricants that are more compatible with engines equipped with particulate traps.

### **SUMMARY OF THE INVENTION**

Therefore, in accordance with a first aspect of the invention, there is provided a lubricating oil composition used in, or for use in, a compression ignited (diesel) internal combustion engine operated with diesel fuel having a sulphur content of less than 50 ppm, preferably less than 30 ppm, more preferably less than 15 ppm, such as less than 10 ppm, said lubricating oil composition comprising a major amount of oil of lubricating viscosity, and a minor amount of at least one metal-containing detergent, wherein said lubricating oil composition has a total ash content of less than 1.0 wt. %, preferably less than 0.8 wt. %, such as less than 0.7 wt. %, more preferably less than 0.6 wt. %, based on the total weight of the lubricating oil composition.

In an embodiment of the first aspect, the total amount of ash contributed to said lubricating oil composition by said at least one metal-containing detergent is from 0 to less than 0.9 wt. %, preferably less than 0.8 wt. %, more preferably less than 0.7 wt.

%, such as less than 0.6 wt. %, based on the total weight of the lubricating oil composition.

5 In accordance with a second aspect of the invention, there is provided a lubricating oil composition used in, or for use in, a spark ignited (gasoline) internal combustion engine operated with gasoline having a sulphur content of less than 50 ppm, preferably less than 30 ppm, more preferably less than 15 ppm, such as less than 10 ppm, said lubricating oil composition comprising a major amount of oil of lubricating viscosity, and a minor amount of at least one metal-containing detergent,  
10 wherein said lubricating oil composition has a total ash content of less than 0.7 or less than 0.65 %, preferably less than 0.6 wt. %, more preferably less than 0.5 wt. %, such as less 0.4 wt. %, based on the total weight of the lubricating oil composition.

15 In an embodiment of the second aspect, the total amount of ash contributed to said lubricating oil composition by said at least one metal-containing detergent is from 0 to less than 0.6 or less than 0.55 wt. %, preferably less than 0.5 wt. %, more preferably less than 0.4 wt. %, such as less than 0.3 wt. %, based on the total weight of the lubricating oil composition.

20 In an embodiment, independently of other embodiments, of either the first or second aspect, said at least one metal-containing detergent comprises, and preferably consists essentially of, at least one salicylate detergent.

25 In accordance with a third aspect of the invention, there is provided a compression ignited (diesel) internal combustion engine operated with diesel fuel having a sulphur content of less than 50 ppm, preferably less than 30 ppm, more preferably less than 15 ppm, such as less than 10 ppm and lubricated with a lubricating oil composition as defined in the first aspect.

30 In accordance with a fourth aspect of the invention, there is provided a spark ignited (gasoline) internal combustion engine operated with gasoline having a sulphur content of less than 50 ppm, preferably less than 30 ppm, more preferably less than 15

ppm, such as less than 10 ppm and lubricated with a lubricating oil composition as defined in the second aspect.

5 In accordance with a fifth aspect of the invention, there is provided a method of operating a compression ignited (diesel) internal combustion engine, which method comprises operating said engine with a fuel having a sulphur content of less than 50 ppm, preferably less than 30 ppm, more preferably less than 15 ppm, such as less than 10 ppm, and lubricating said engine with a lubricating oil composition as defined in the first aspect.

10

In accordance with a sixth aspect of the invention, there is provided a method of operating a spark ignited (gasoline) internal combustion engine, which method comprises operating said engine with a fuel having a sulphur content of less than 50 ppm, preferably less than 30 ppm, more preferably less than 15 ppm, such as less than 15 10 ppm, and lubricating said engine with a lubricating oil composition as defined in the second aspect.

20 In accordance with a seventh aspect of the invention, there is provided a use of a lubricating oil composition as defined in either the first or second aspect to reduce the amount of particulate ash generated by consumption of metal-containing lubricant additives during operation of a lubricated internal combustion engine operated with a fuel having a sulphur content of less than 50 ppm, preferably less than 30 ppm, more preferably less than 15 ppm, such as less than 10 ppm.

25 In accordance with an eighth aspect of the invention, there is provided the use of a lubricating oil composition as defined in either the first or second aspect to reduce corrosion in an internal combustion engine operated with a fuel having less than 50 ppm of sulphur, preferably less than 30 ppm, more preferably less than 15 ppm, such as less than 10 ppm.

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In accordance with another aspect of the invention, there is provided a combination of (i) a fuel having less than 50 ppm of sulphur, preferably less than 30

ppm, more preferably less than 15 ppm, such as less than 10 ppm, and (ii) a lubricating oil composition as defined in the first or second aspect, in an internal combustion engine, such as a compression- or spark-ignited engine.

5           The features of the invention will now be discussed in more detail.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

10           Figure 1 shows graphically the amount of NO<sub>x</sub> and SO<sub>x</sub> gas in the exhaust gas, as measured during the Mack T10 engine test with and without an exhaust gas recirculation device, which engine was fuelled with 400ppm of sulfur fuel.

15           Figure 2 shows graphically a comparison between TBN depletion and TAN increase for low ash lubricating oil compositions in engines operated with high and low sulphur content fuels.

            Figure 3 compares graphically the lead corrosion profile of lubricating oil compositions containing phenate/sulfonate detergents and salicylate detergents.

20           Figure 4 compares graphically TBN depletion and TAN increase profiles for lubricating oil compositions containing phenate/sulfonate detergents and salicylate detergents.

### **DETAILED DESCRIPTION OF THE INVENTION**

25           As described in the above aspects, the invention is applicable to all internal combustion engines including both spark-ignited (gasoline fueled) and compression-ignited (diesel fueled) internal combustion engines.

30           In an embodiment, the present invention is particularly applicable to internal combustion engines provided with a particulate trap or an exhaust gas recirculation (EGR) system or both particulate trap and an exhaust gas recirculation (EGR) system. In the event that the engine is provided with an EGR system the exhaust gases and/or

combustion air is/are preferably cooled prior to introduction into the engine combustion chamber.

Preferably, the internal combustion engine is a passenger car diesel engine (PCD) or heavy duty diesel (HDD) engine, more particularly a PCD or HDD engine provided with a particulate trap.

Fuels, whether gasoline or diesel fuel, useful in the practice of the invention have a sulphur content below 50 ppm, preferably below 30 ppm, more preferably below 15 ppm, such as below 10 ppm. In an embodiment, the sulphur content of the fuel is at least 5 ppm. The level of sulphur may be determined using various methods including X-ray (ASTM D2622-1) or UV (ASTM D5453-93). Such fuels may comprise saturated, olefinic and aromatic hydrocarbons or mixtures thereof. Such fuels can be derived from straight run streams, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions, catalytically reformed hydrocarbons or synthetically produced hydrocarbon mixtures, such as those derived from methane. The sulphur content of fuels containing sulphur can be reduced by known methods, such as, for example, catalytic hydrodesulphurization.

The oils of lubricating viscosity useful in the practice of the invention may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gasoline engine oils, mineral lubricating oils and heavy duty diesel oils. Generally, the viscosity of the oil ranges from about 2 mm<sup>2</sup>/sec (centistokes) to about 40 mm<sup>2</sup>/sec, especially from about 3 mm<sup>2</sup>/sec to about 20 mm<sup>2</sup>/sec, most preferably from about 4 mm<sup>2</sup>/sec to about 10 mm<sup>2</sup>/sec, as measured at 100°C.

Natural oils include animal oils and vegetable oils (*e.g.* castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.



Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (*e.g.* polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes  
5 (*e.g.* dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (*e.g.* biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof.

10 Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (*e.g.* methyl-  
15 polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>-C<sub>8</sub> fatty acid esters and C<sub>13</sub> Oxo acid diester of tetraethylene glycol.

20 Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (*e.g.* phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (*e.g.* butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-  
25 ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with  
30 two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C<sub>5</sub> to C<sub>12</sub> monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

5        Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl)silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and  
10 poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (*e.g.* tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and re-refined oils can be used in lubricants of the present  
15 invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from an esterification and used without further treatment would be an unrefined oil. Refined oils are similar to unrefined oils except that the oil  
20 is further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to provide refined oils but begin with oil that has already been used in service. Such re-refined oils are also  
25 known as reclaimed or reprocessed oils and are often subjected to additionally processing using techniques for removing spent additives and oil breakdown products.

The oil of lubricating viscosity may comprise a Group I, Group II, Group III, Group IV or Group V base stocks or base oil blends of the aforementioned base  
30 stocks. Preferably, the oil of lubricating viscosity is a Group II, Group III, Group IV or Group V base stock, or a mixture thereof, or a mixture of a Group I base stock and one or more a Group II, Group III, Group IV or Group V base stock. The base stock,

or base stock blend preferably has a saturate content of at least 65%, more preferably at least 75%, such as at least 85%. Most preferably, the base stock, or base stock blend, has a saturate content of greater than 90%. Preferably, the oil or oil blend itself will have a sulphur content of less than 0.5%, preferably less than 0.05%, more  
5 preferably less than 0.03%, by weight. The sulphur content of oil or oil blend is preferably zero, more preferably at least 0.005 weight %.

Preferably the volatility of the oil or oil blend, as measured by the Noack test (ASTM D5880), is less than or equal to 30%, preferably less than or equal to 25%,  
10 more preferably less than or equal to 20%, most preferably less than or equal 16%.

Preferably, the viscosity index (VI) of the oil or oil blend is at least 85, preferably at least 100, most preferably from about 105 to 140.

15 Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

20

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index between 80 and 120;

25

b) Group II base stocks contain at least 90 percent saturates and no more than 0.03% sulphur and have a viscosity index between 80 and 120;

c) Group III base stocks contain at least 90 percent saturates no more than 0.03% sulphur and have a viscosity index between 80 and 120;

30

d) Group IV base stocks are polyalphaolefins (PAO).

e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Table 1 - Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

5

Metal-containing or ash-forming detergents function as both detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail. The polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base may be incorporated by reacting excess metal compound (*e.g.* an oxide or hydroxide) with an acidic gas (*e.g.* carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (*e.g.* carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically will have a TBN of from 250 to 450 or more.

20 Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulphurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, *e.g.* barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which  
25 may both be present in detergents used in a lubricant, and mixtures of calcium and/or

magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450, neutral and overbased calcium phenates and sulphurized phenates having TBN of from 50 to 450 and neutral and overbased magnesium or calcium salicylates having a TBN of from 20 to 450.

- 5 Combinations of detergents, whether overbased or neutral or both, may be used.

Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons.

- 10 Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkylaryl sulfonates usually contain from about 9 to about 80 or  
15 more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

- The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides,  
20 nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 wt. % (preferably at least 125 wt. %) of that stoichiometrically required.

- Metal salts of phenols and sulphurized phenols are prepared by reaction with an  
25 appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulphurized phenols may be prepared by reacting a phenol with sulphur or a sulphur containing compound such as hydrogen sulfide, sulphur monohalide or sulphur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged  
30 by sulphur containing bridges. Alkylene bridged phenols are also suitable for use as metal phenates.

Carboxylate detergents, *e.g.* salicylates, can be prepared by reacting an aromatic carboxylic acid with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain

5 heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected *via* alkylene bridges. The carboxylic moiety may be attached directly or

10 indirectly to the aromatic moiety. Preferably the carboxylic acid group is attached directly to a carbon atom on the aromatic moiety, such as a carbon atom on the benzene ring. More preferably, the aromatic moiety also contains a second functional group, such as a hydroxy group or a sulfonate group, which can be attached directly or indirectly to a carbon atom on the aromatic moiety.

15

Preferred examples of aromatic carboxylic acids are salicylic acids and sulphurized derivatives thereof, such as hydrocarbyl substituted salicylic acid and derivatives thereof. Processes for sulphurizing, for example a hydrocarbyl - substituted salicylic acid, are known to those skilled in the art. Salicylic acids are

20 typically prepared by carboxylation, for example, by the Kolbe - Schmitt process, of phenoxides, and in that case, will generally be obtained, normally in a diluent, in admixture with uncarboxylated phenol.

Preferred substituents in oil - soluble salicylic acids are alkyl substituents. In

25 alkyl - substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility.

30 Detergents generally useful in the formulation of lubricating oil compositions also include "hybrid" detergents formed with mixed surfactant systems, *e.g.* phenate/salicylates, sulfonate/phenates, sulfonate/salicylates,

sulfonates/phenates/salicylates, as described, for example, in pending U.S. Patent Application Nos. 09/180,435 and 09/180,436 and U.S. Patent Nos. 6,153,565 and 6,281,179 and EP 0 750 659.

5            Preferably, the metal-containing detergent, present in the lubricating oil compositions of the invention, comprises, preferably consists essentially of, at least one salicylate detergent. It is preferred that the detergent consists essentially of a calcium salicylate having a TBN of less than 80 and another calcium salicylate having a TBN greater than 150.

10

          Surprisingly, it has been found that, in engines operated by low-sulphur (less than 50 ppm) fuels, the amount of detergent needed to provide detergency and acid neutralization can be reduced from conventional amounts. Specifically, it has been found that in diesel engines operated by low-sulphur (less than 50 ppm) fuels, an  
15        amount of detergent contributing from 0 to less than 0.9 wt. %, preferably less than 0.8 wt. %, more preferably less than 0.7 wt. %, such as less than 0.6 wt % of ash to the lubricating oil composition is preferably sufficient to provide detergency and acid neutralization; in an embodiment the amount is zero ash, *i.e.* no metal-containing detergents, preferably at least 0.1 wt% of ash is derived from the metal containing  
20        detergent(s).

          In gasoline engines operated by low-sulphur (less than 50 ppm) fuels, it has been found that an amount of detergent contributing from 0 to less than 0.6 or less than 0.55 wt. %, preferably less than 0.5 wt. %, more preferably less than 0.4 wt. %,   
25        such as less than 0.3 wt %, of ash to the lubricating oil composition is preferably sufficient to provide detergency and acid neutralization; in an embodiment the amount is zero ash, *i.e.* no metal-containing detergents, preferably at least 0.1 wt% of ash is derived from the metal containing detergent(s).

30            This is in contrast to conventional lubricating oil compositions for engines operated by high sulphur fuels, which generally require amounts of detergent contributing more than 1.0 wt. % of ash for diesel engine lubricating oil compositions

and more than 0.6 wt. % of ash for gasoline engine lubricating oil compositions. Ash content expressed as "sulfated ash" or "SASH" can be determined by the methods of ASTM D874.

5           It is not unusual to add a detergent or other additive, to a lubricating oil, or additive concentrate, in a diluent, such that only a portion of the added weight represents an active ingredient (A.I.). For example, detergent may be added together with an equal weight of diluent in which case the "additive" is 50% A.I. detergent. As used herein, the term weight percent (wt. %), when applied to a detergent or other  
10       additive refers to the weight of active ingredient.

          The use of reduced amounts of metal-containing detergents allows for the formulation of lower ash content lubricating oil compositions. Preferably, the total ash content of the lubricating oil composition of the present invention is less than 0.9  
15       wt. %, preferably less than 0.8 wt. %, such as less than 0.7 wt. %, more preferably less than 0.6 wt. %, such as less than 0.5 wt. % for lubricating oil formulated for diesel engines. In an embodiment, the lubricating oil formulated for diesel engines has zero ash, *i.e.* no metal-containing additives, more preferably at least 0.1 weight  
20       t%, based on the weight of the lubricating oil composition.

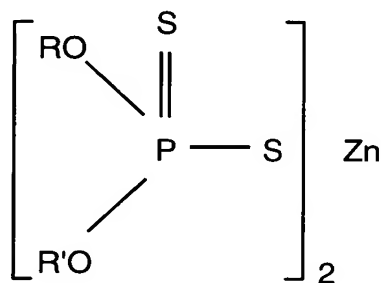
          For gasoline engines, the total ash content of the lubricating oil composition of the present invention is preferably less than 0.65 wt. %, preferably less than 0.6 wt. %, such as less than 0.5 wt. %, such as less than 0.4 wt. %, based on the total weight of the lubricating oil composition. In an embodiment, the lubricating oil formulated  
25       for gasoline engines has zero ash, *i.e.* no metal-containing additives, more preferably at least 0.1 weight t%, based on the weight of the lubricating oil composition.

          Major sources of additive ash other than metal-containing detergents, include metal-containing antioxidant and/or antiwear agents, such as dihydrocarbyl  
30       dithiophosphate metal salts. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are conventionally used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt.



%, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with  $P_2S_5$  and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid can be made by reacting a mixture of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

The preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. Preferably, the amount of dihydrocarbyl dithiophosphate metal salt is reduced concurrent with the amount of metal-containing

detergent such that the dihydrocarbyl dithiophosphate metal salt and other metal-containing additives introduces no more than 0.1 wt. % to about 0.15 wt. % of ash into the lubricating oil composition. The present invention may be particularly useful when the lubricant phosphorus level is from 0 to about 0.12 wt. %, preferably from  
5 about 0.03 to about 0.10 wt. %. More preferably, the phosphorous level of the lubricating oil composition will be less than about 0.08 wt. %, such as from about 0.05 to about 0.08 wt. %, as determined by the method of ASTM D5185.

As noted above, environmental concerns and expected future oil specification  
10 requirements have also dictated that the overall sulphur level of the lubricant be reduced. Preferably, lubricating oil compositions of the present invention contain no more than 0.5 wt. %, preferably no more than 0.3 wt. %, most preferably no more than 0.2 wt. % of sulphur, based on the total weight of the lubricating oil composition. In an embodiment, the lubricating oil composition contains at least 0.05, such as at  
15 least 0.1, wt % of sulphur, as determined by the method of ASTM D5185.

Sulphur is contributed both by the base oil and certain lubricant additives. Thus, to provide the preferred sulphur levels, in addition to selecting low sulphur base oils (or sulphur-free base oils), the use of sulphur-containing additives should be  
20 minimized or avoided where possible. A reduction in the amount of ZDDP to reduce phosphorus content will also reduce the sulphur content of the lubricating oil composition. In addition, reduced sulphur requirements favors the use of salicylate detergents, which are sulphur-free, over phenate and sulfonate detergents.

Table 2 - Additive Contribution to Formulation Sulphur

Component	Approx % of sulphur contribution to oil composition
ZDDP (0.12%P)	0.24-0.28
ZDDP (0.05%P)	0.10-0.12
Detergent (PC-9) Salicylate	0.00
Phenate/Sulphonate	0.07-0.09
Diluent Oils VM/Components	0.04-0.06

Additional additives may be incorporated into the compositions of the invention to enable particular performance requirements to be met. Examples of additives which may be included in the lubricating oil compositions of the present invention are ashless dispersants, metal rust inhibitors, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, ashless friction modifiers, anti-foaming agents, ashless anti-wear agents and pour point depressants, some of which are described below. These additives, where ashless (metal-free) do not bear on the present invention. Where other metal-containing additives are used, *e.g.* organo-molybdenum antioxidant/antiwear agents, it is preferable to control the amount thereof and use, where possible, alternate, metal-free additives.

The ashless dispersant comprises an oil soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often *via* a bridging group. The ashless dispersant may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

5

Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4 thiadiazoles such as those described in  
10 U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Patent Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in UK Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of  
15 additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 wt. % active ingredient.

Oxidation inhibitors or antioxidants reduce the tendency of base stocks to deteriorate in service which deterioration can be evidenced by the products of  
20 oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C<sub>5</sub> to C<sub>12</sub> alkyl side chains, calcium nonylphenol sulfide, ashless oil soluble phenates and sulphurized phenates, phosphosulphurized or sulphurized hydrocarbons, alkyl substituted diphenylamine,  
25 alkyl substituted phenyl and naphthylamines, phosphorus esters, metal thiocarbamates, ashless thiocarbamates and oil soluble copper compounds as described in U.S. 4,867,890. Most preferred are the alkyl-substituted diphenylamines.

Pour point depressants, otherwise known as lube oil flow improvers, lower the  
30 minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of additives that improve the low temperature fluidity of the

fluid are C<sub>8</sub> to C<sub>18</sub> dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

Foam control can be provided by many compounds including an antifoamant of  
5 the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

A small amount of a demulsifying component may be used. A particularly  
suitable demulsifying component is described in EP 330,522. It is obtained by  
reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a  
10 polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass  
% active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is  
conventional.

The viscosity modifier (VM) functions to impart high and low temperature  
15 operability to lubricating oil. Suitable viscosity modifiers are polyisobutylene,  
copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates,  
polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated  
dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters,  
and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and  
20 isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene  
and isoprene and isoprene/divinylbenzene.

Some of the above-mentioned additives can provide a multiplicity of effects;  
thus for example, a single additive may act as a dispersant-oxidation inhibitor.  
25 Multifunctional viscosity modifiers that also function as dispersants are also known.  
The use of multifunctional additives is well known and does not require further  
elaboration.

When lubricating compositions contain one or more of the above-mentioned  
30 additives, each additive is typically blended into the base oil in an amount that enables  
the additive to provide its desired function. Representative effective amounts of such  
additives (excluding metal detergents and metal dihydrocarbyl dithiophates, which are

discussed above), when used in crankcase lubricants, are listed below. All the values listed are stated as mass percent active ingredient.

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
Dispersant	1 - 10	1 - 7
Corrosion Inhibitor	0 - 5	0 - 1.5
Antioxidant	0 - 5	0.01 - 3
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Antifoaming Agent	0 - 5	0.001 - 0.15
Supplemental Antiwear Agents	0 - 1.0	0 - 0.5
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 10	0.25 - 3
Basestock	Balance	Balance

5            Preferably, the Noack volatility of the fully formulated lubricating oil composition (oil of lubricating viscosity plus all additives) will be no greater than 15, such as no greater than 13, preferably no greater than 10, such as no greater than 8 wt. %, as measured by ASTM 5880.

10           In a preferred embodiment, the lubricating oil composition of the present invention is a multigrade lubricating oil composition in the form of an SAE 15W-X, SAE 10W-X, SAE 5W-X or 0W-X composition, wherein X represents any one of 20, 30 and 40. Preferably, the oil composition is in the form of an SAE 5W-X or 0W-X when used in a gasoline engine, and the oil composition is in the form of an SAE  
15   15W-X or 10W-X when used in a diesel engine. Advantageously, X represents either 30 or 40, especially 30. The properties of multigrades are defined in the Society of Automotive Engineers document SAE J300.

             It may be desirable, although not essential, to prepare one or more additive  
20   concentrates comprising additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition.

The final composition may employ 5 to 25 mass %, preferably 5 to 18 mass %, typically 10 to 15 mass % of the concentrate (based on active ingredient), the remainder being oil of lubricating viscosity.

5           In this specification:

          The term "hydrocarbyl" as used means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule *via* a carbon atom, but does not exclude the presence of other atoms or  
10       groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group.

          The term "comprising" or "comprises" means the presence of stated features, integers, steps or components, but does not preclude the presence or addition of one or  
15       more other features, integers, steps, components or groups thereof. In the instance the term "comprising" or "comprises" is used herein, the term "consisting essentially of" and its cognate are within its scope and are a preferred embodiment of it, and consequently the term "consisting of" and its cognate are within the scope of "consisting essentially of" and are a preferred embodiment of it.

20

          The term "oil-soluble" or "oil-dispersible" does not mean that the compounds are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. They do mean, however, that the compounds are, for instance, soluble or stable dispersible in the oil to an extent sufficient to exert their intended effect in the  
25       environment in which the composition is employed. Moreover, the additional incorporation of other additives such as those described above may affect the solubility or dispersibility of the compounds.

          The term "major amount" means in excess of 50 mass % of the composition.

30

          The term "minor amount" means less than 50 mass % of the composition.

This invention will be further understood by reference to the following examples, wherein all parts are parts by weight, unless otherwise noted and which include preferred embodiments of the invention.



## **EXAMPLES**

Lubricant comprising conventional additives, metal-containing detergents and a ZDDP component were prepared by methods known in the art. Table 3 provides the characteristics of the lubricants used in the Mack T10 engine test. The lubricants in Table 3 were blended to SAE 15W-40 viscometric grade.

The Mack T10 engine test developed for the API CI-4 category was used to examine the bearing lead corrosion, ring and liner wear performance of reduced ash lubricants also containing reduced levels of phosphorus and sulphur. The standard Mack T10 test method incorporating EGR was used, however the tests were run on a non-automated stand. The fuel sulphur level was varied during the experiments from 400 ppm to 15 ppm. All rated parameters were reported in the normal manner with the exception that an overall merit was not established.

15

A summary of the results obtained is given in Table 4. It is clear from the data of Table 4 that a reduction in both phosphorus and more particularly the ash content of the lubricant is possible when using low sulphur fuel. Passing lead corrosion performance was achieved at ash levels as low as 0.6% in combination with a phosphorus content of 0.06% when using 15ppm sulphur fuel. Testing has demonstrated that fuel sulphur, even at the relatively low concentration of 400 ppm, is a major contributor to mineral acid formation, TBN (total base number) depletion, and hence lubricant ash requirement. This was surprising as it was considered that the nitric and nitrous acids formed *via* NO<sub>x</sub> gas hydrolysis would have played a far more dominant role in terms of TBN depletion. The introduction of low sulphur fuel for after-treatment durability is also consistent with the formulation of reduced ash lubricants to meet diesel particulate filter (DPF) requirements.

It is likely that testing using the Mack T10 in the presence of EGR represents a worst case scenario in terms of ash requirement, TBN depletion and lead corrosion for meeting the expected requirements of the PC-10 specification. The use of NO<sub>x</sub> reduction after-treatment devices to meet US Tier III legislation could result in the

30

removal of EGR from the engine design or more likely the use EGR systems operated at lower recirculation rates. The incorporation of particulate traps into US Tier III emission solutions and their requirement for reduced ash formulations, would appear feasible with the introduction of a 15 ppm sulphur limit in 2006.

5

Table 3 – Characteristics of the Lubricants

	Units	Typical PC-9 Oil	Oil A	Oil B	Oil C	Oil D	Oil E
Phosphorus	wt. %	0.12	0.06	0.06	0.06	0.06	0.06
Sulphur	wt. %	0.6	0.2	0.2	0.19	0.13	0.14
Lubricant ash	wt. %	1.2	1.0	1.0	0.75	0.75	0.6
Ash contributed by detergent(s)	wt. %	0.95	0.95	0.95	0.67	0.64	0.38
TBN (D2896)	mgKOH/g	10.0	9.1	9.1	7.2	7.3	5.9

Table 4 - Mack T10 Lead Corrosion Performance Results

	CI-4 Limit	Typical PC-9 Oil	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Lubricant used	-	-	A	B	C	D	E
Fuel sulphur, ppm	-	400	400	15	15	15	15
EOT Pb*, ppm	35	25	10**	19	24	15	27
ΔPb 250-300 hrs, ppm	14	10	-	9	9	6	9

\*End Of Test lead

\*\*Test terminated at 220 hours owing to a mechanical fault

10

The effect of fuel sulphur level on TBN depletion is illustrated graphically in Figure 2. The TBN depletion and TAN (total acid number) increase profiles for oils A and B are given. Oils A and B are in fact back-to-back runs of the same lubricant tested using high (400 ppm) and low (15 ppm) sulphur fuel, respectively. The TBN depletion profile when testing with 400 ppm sulphur fuel is typical of a PC-9 oil. TBN and TAN commonly cross between 150-200 hours. Approximately fifty to seventy five hours after the cross-over point, lead corrosion begins to increase significantly. In contrast, when 15 ppm sulphur fuel is used, TBN and TAN do not cross for the entirety of the 300 hour test.

15

20

Oils C and D compare the performance of phenate/sulphonate detergents with salicylate based detergents in typical PC-9 lubricating oil formulations. The oils were matched for ZDDP, TBN and soap content. The sulphur content of the salicylate formulation (Oil D) is lower than that of the phenate/sulphonate formulation (Oil C) as the salicylate detergent is sulphur free. Both chemistry types provide passing performance, however, the data suggest that lead corrosion performance is superior for the salicylate chemistry. Figure 3 illustrates the lead corrosion profile with test duration for the two test oils. The technical justification for this performance difference can be found by comparing the TBN depletion and TAN increase profiles of the two lubricants. Such a comparison is made in Figure 4. The TBN depletion for the salicylate oil is markedly reduced in comparison to that of the phenate/sulphonate oil. A possible explanation for this reduced TBN depletion is that the salicylate oil neutralises acid present less effectively. However, if this were the case, a more rapid increase in TAN would be expected together with inferior corrosion performance. In contrast, the TAN increase for the salicylate oil is comparable to that of the phenate/sulphonate oil. The superior performance of salicylate detergent allows for the formulation of lower ash lubricating oil compositions.

The performance of the detergent in the low ash lubricating oil compositions of the present invention was determined in passenger car diesel engines operated with both high (400 and 3000 ppm) and low (10 ppm) sulphur fuels using an OM 602A engine test (CEC L-051-A-9A).

The piston cleanliness performance of lubricating oil compositions of the present invention was evaluated in passenger car diesel engines operated with low (10 ppm) and high (400 ppm and 3000 ppm) sulphur diesel fuels. All the tested compositions (Oils F to G) were SAE 5W-30 grade and contained comparable additives including identical salicylate detergents. The characteristics of the lubricating oil compositions and fuels used, and the results obtained, are set forth in Table 5.

Table 5 – Characteristics of the lubricating oil compositions and fuel, and  
OM602A engine test results

	Ex. 6	Ex. 7	Ex. 8	Lower Limit For Passing
Lubricant	F	G	H	--
Phosphorus, wt. %	0.06	0.05	0.05	--
Lubricant ash, wt. %	0.56	0.50	0.50	--
Ash contributed by detergent (s), wt. %	0.35	0.39	0.38	--
Fuel sulphur, ppm	10	400	3000	--
Piston Merit (avg.)	32.1	26.0	22.8	24

The above-data demonstrate the ability of lubricating oil compositions  
5 formulated with amounts of detergent contributing reduced amounts of ash to  
maintain piston cleanliness at acceptable levels in engines operated with low sulphur  
fuels.

The disclosures of all patents, articles and other materials described herein are  
10 hereby incorporated, in their entirety, into this specification by reference.

Compositions described as "comprising" a plurality of defined components are  
to be construed as including compositions formed by admixing the defined plurality  
of defined components The principles, preferred embodiments and modes of  
15 operation of the present invention have been described in the foregoing specification.  
What applicants submit is their invention, however, is not to be construed as limited  
to the particular embodiments disclosed, since the disclosed embodiments are  
regarded as illustrative rather than limiting. Changes may be made by those skilled in  
the art without departing from the spirit of the invention.